# AD NUMBER

AD879156

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# AUTHORITY

ONR ltr, 13 Jan 1972

HPC 70-121

# MONSANTO/WASHINGTON UNIVERSITY
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# CONTROLLED ORIENTATION OF DISCONTINUOUS FIBERS IN COMPOSITES

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DECEMBER 1970

MONSANTO/WASHINGTON UNIVERSITY ASSOCIATION
HIGH PERFORMANCE COMPOSITES PROGRAM
SPONSORED BY ONR AND ARPA
CONTRACT NO. N00014-67-C-0218, ARPA ORDER 876
ROLF BUCHDAHL, PROGRAM MANAGER



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FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-48 /4-13-66, entitled "Development of High Performance Composites."

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl. (Phone: Area Code 314-694-4721).

The contract is funded for $7,000,000 and expires 30 April 1972.

# CONTROLLED ORIENTATION OF DISCONTINUOUS FIBERS IN COMPOSITES

T. L. Tolbert

ABSTRACT

Yarns of unidirectionally oriented, discontinuous high-modulus fibers and whiskers have been successfully produced in the laboratory by a modified vortex spinning process. Both core yarns in which the higher modulus fibers are overwrapped with organic or small diameter glass fibers and all-whisker-yarns have been spun. These yarns can be readily incorporated into plastics as reinforcing agents by filament winding and related procedures. The strength of resulting composites is markedly superior to those of similar materials fabricated by other techniques due to well controlled fiber orientation and very uniform fiber overlap.

# CONTROLLED ORIENTATION OF DISCONTINUOUS FIBERS IN COMPOSITES

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The tremendous potential of high modulus fibers and whiskers as reinforcing agents for plastics and metals is now well recognized. In a little more than a decade, use of such materials has advanced from laboratory studies aimed primarily at extending glass fiber reinforced plastics technology, or imitating naturally occurring fiber reinforced systems, to commercial manufacture and acceptance of resulting composites as practical engineering materials. Composites containing high modulus fibers such as boron and graphite are currently employed as primary and secondary structure in such diverse applications as components for military and commercial aircraft, sports equipment and advanced prosthetic devices.

Key to the almost explosive growth of the composites field has been development of effective methods for producing and utilizing high modulus fibers. Small scale manufacture of continuous fibers such as boron and graphite fiber was achieved quite early and production of high quality fiber made routine. More recently, procedures for much larger scale operation have been developed which promise to reduce cost and make use of composites reinforced with these fibers generally practical for

many engineering applications. Methods for fabricating boron and graphite fiber mat composites, once primarily hand operations, have been greatly improved and to some extent automated and reliable procedures worked out for incorporating and composites into component structure. Utilization of boron and graphite composites thus now appears more limited by shortcomings in matrix performance and in design methodology than by deficiencies of the fibers.

Significant advances have also been made in employment of whisker fibers as reinforcing agents, although overall progress has not been as great as with boron and graphite. The concept of using monocrystalline fibers as reinforcing agents is extremely attractive, of course, and so has been the subject of some excellent research, especially in the U.K. Good progress has been made in solving problems related to whisker fiber quality, in scaling-up manufacture and even in bringing the price of such materials to practical levels. For example, Norton Research Corporation, Cambridge, Mass., North American Licensee of the Phillips AG Silicon Carbide Whisker Process, is said to have under development a process for producing extremely uniform good quality whiskers on a pilot scale at projected commercial prices of less than $50.00 per pound. Unfortunately, however, progress toward utilizing whiskers as reinforcing agents has

been much slower; practical methods are still needed for converting whiskers and resin into high performance composites.

As single crystals, whiskers exhibit equivalent moduli and far higher strengths than other fibers of similar composition. It was the strength of these fibers, often more than a million psi, that initially generated so much enthusiasm for the idea of whisker reinforced systems. Exploiting this is another matter, however; whisker strength has proved to be extremely difficult to translate into composite strength. Unlike boron filament and graphite fibers, whiskers currently are produced only in discontinuous form and are usually extremely small in size, often only a few microns in diameter and a few millimeters long. Both factors greatly complicate the problem of controlling directional orientation, placement, overlap and distribution of the fibers in composites to the degree necessary for good reinforcement efficiency, and hence good composite properties. Control of fiber orientation has proved particularly difficult. As would be expected, these problems are not limited to whiskers, but also have been encountered in attempts to employ a variety of other small diameters discontinuous fibers as reinforcing agents.

A number of approaches to overcoming these fabrication problems have been reported, the two most effective being in-situ growth of reinforcing whiskers in a metallic matrix and flow

orientation of short, high modulus fibers in a viscous, coagulable resin. The latter approach, pioneered with whisker adn asbestos reinforced systems by workers at the Explosives Research and Development Establishment, Waltham Abbey, Exxex, England, has proved particularly versatile. Strands of oriented fibers suitable for subsequent processing can be prepared in this way by "wet spinning" techniques[1-4] or, at the other extreme, finished composites in which the fibers are flow oriented can be prepared directly by modified injection molding procedures.[5] Unfortunately, these techniques are not suitable for processing high modulus fibers greater in length than about 10 mm, and so development of an alternate method for handling these materials has been necessary. The technique found most successful in studies conducted by the Monsanto/Washington University Association is based on a textile process, "vortex" or "open end" spinning; this is described below.

## Spinning of Whisker Fiber Yarns

Impetus for development of an alternate method for processing discontinuous high modulus fibers, such as whiskers, into composites came in our program from a study on the reinforcement efficiency of such fibers. Long staple (10-30 mm) β-silicon carbide whiskers had been made available for the work, but no satisfactory method was available for converting them into the required unidirectionally reinforced plastic specimens.

While flow orientation techniques were quite satisfactory for preparing directionally reinforced composites from short fibers, scuh an approach could not be employed with the longer material due to excessive breakage of fibers caused by the high shear forces generated in these systems. Following the lead of several earlier workers[6,7] in the U.S.A., attention was given instead to study of several textile processes which might be modified to produce resin-free "packages" or yarns of axially oriented fibers suited to filament winding and related composite fabrication procedures. The most promising of these proved to be a form of "vortex" or "open end" spinning.

Initially, a simple laboratory vortex spinner, similar in principle to that developed by Strang[8] for textile yarns, was used to prepare yarns containing whisker fibers entrapped among helically twisted textile (binder) fibers. In this, fibers dispersed in a viscous medium were formed into a strand by the action of hydrodynamic forces on the suspension as it passed through a rapidly rotating tube in the spinner head. The yarn was collected as it emerged from the tube assembly, washed free of the suspending liquid (usually corn syrup for convenience) in a gentle stream of solvent, and taken up on a rotating drum. Yarns were reasonably uniform and, even though the binder fibers were un-

crimped, of sufficient strength for composite preparation. Unfortunately, however, axial orientation of the entrapped whisker fibers was quite imperfect due to a tendency of the whiskers to follow the helical path of the binder material. In addition, fiber breakage was excessive.

Modification of the first apparatus to permit introduction of whiskers as a separate, more viscous suspension at the center of the flowing binder fiber suspension prior to entry to the rotating tube assembly proved a more satisfactory approach. Fluid forces are not great enough in the central region of the suspension to disturb orientation or cause breakage of the whiskers as they are introduced, compacted and wrapped by the binder material. Resulting yarns, consisting of a core of axially oriented whiskers helically wrapped by a thin layer of textile fibers, are uniform and strong enough for easy handling. Whisker breakage is minimal.

The modified spinning apparatus is shown in Fig. 2. It consists of a vertically mounted vortex spinning assembly fed under nitrogen pressure from spearate holding tanks for the fiber slurries. The spinning assembly is basically like that in the previous apparatus except that a short portion of the spinning barrel immediately below the rotating tube is expanded

to approximately twice the original diameter to provide a chamber for combining fiber slurries. In our particular system, core slurry is introduced through a 6 mm tube, just below the rotating tube assembly, into the center of a 16 mm slurry chamber. The slurry chamber and core slurry tube are connected directly to the holding tanks by tubing entering through the top of the tanks and ending in a conically flared tip about 12 mm above the bottom. Lids of the tanks are fastened with bolts and are sealed with rubber "O" rings capable of withstanding 100 psi pressure. In operation, the speed of the rotating tube and the rate of slurry flow are controlled (annular flow must exceed core flow) so that the fibers twist together in the short converging section of the chamber, rather than in the spinning barrel proper, since in this region the outer fibers approach the core from a non-axial postion and are wrapped more uniformly around the core.

The speed at which the rotating tube of the spinner head must turn in order to impart enough twist for good yarn strength varies with each system, depending primarily on the flow rates of the slurries, slurry viscosities and the mechanical properties of the fibers. With our apparatus, rotational rates ranging from 1200-1700 rpm produce sufficient twist in most cases for yarn take-up velocities of several inches per second. Faster spinning is eadily possible but requires more precise control of variables.

Due to the high cost of whiskers, various glass fibers were used as model materials in developing the spinning apparatus and in all process studies. See Table 1. These proved to be excellent substitutes for whiskers; no difficulties were encountered in switching the spinning operation from one material to the other. Several of the glass fiber yarns also proved to be interesting in their own right. It was found, for example, that the diameter of Beta glass fibers is small enough, and fiber flexibility therefore great enough that these fibers can be used both as wrapping and core materials. Thus, yarns of short "E" glass fibers wrapped with Beta glass fiber and of 100% Beta fiber can be prepared. The textile fibers employed as binder materials included uncrimped acetate, triacetate, high tenacity rayon and Acrilan 57. All were found to be satisfactory for the purpose.

In producing core yarns, approximately equal concentrations of glass or whisker core fiber and of the lower modulus binder fibers were used in the spinning slurries. Maximum concentration was determined by the amount of the binder fibers which could be used since these are the more flexible and exhibit the greater tendency to entangle with resultant loss of dispersion uniformity. For the four binder materials shown in Table 1, the limiting

concentration for 18 mm staple dispersed in corn syrup (100-350 poise) ranged from 0.05 to 0.1 volume percent when the spinning tube of the laboratory equipment was 6 mm in diameter. In order to minimize damage to the fibers, the viscosity of the core slurry was maintained at approximately 100 times that of the annular slurry.

Concentrations of high modulus fibers in the vortex-spun yarns prepared in our studies ranged up to about 36 volumer percent, the degree of axial orientation being very high at all levels. As mentioned, with smaller diameter glass fibers it also was possible to spin 100% glass staple yarns of reasonably good uniformity and strength. Similar, although much weaker, 100% yarns were spun from whisker fibers as well. The supply of whiskers was not sufficient to permit more than a few attempts to prepare such yarns, but results were promising enough that there is little doubt that conditions could be found for producing good quality all-whisker yarns.

Summarizing efforts on whisker yarn preparation, a process has been worked out for converting discontinuous, high modulus fibers into a yarn consisting of a core of these fibers in axially aligned form helically wrapped with lower modulus binder fibers. The yarn is produced by subjecting a

two component suspension, made up of a viscous, laminarly flowing slurry of high modulus fibers urrounded by a more rapidly flowing, less viscous suspension of much lower modulus fibers, to an axial vorticity gradient. The gradient, generated in the suspension by flow through a rotating tube, provides the twisting force required. Core yarns containing up to 36 volume percent of long staple β-silicon carbide whiskers and even higher percentages of glass fiber have been prepared in this way. Strong, relatively uniform textile-like yarns of discontinuous Beta glass fiber alone also have been produced in this way.

Vortex spinning of inorganic fiber core yarns is the only potentially practical approach known to the author by which long staple small diameter high modulus fibers and whiskers can be "packaged" in polymer-free directionally oriented form. While strictly a laboratory technique as practiced here and of doubtful interest for textile applications, this or a related approach could be the key to much larger scale utilization of such fibers as reinforcing agents. Certainly, it is one of the first methods* to make filament winding and related fabrication

*The Canadian "Bobtex" Integrated Composite Spinning process[9] is said to be applicable to some inorganic fibers and so, assuming that these are fibers of interest as reinforcing agents, may be another way of obtaining yarns for composite fabrication. However, since a binder polymer must be presen' in "Bobtex" yarns to supplement the twist-applied forces between fibers, use may be restricted in some systems to composites of relatively low fiber content.

procedures worth considering as means for controlling the directional orientation, placement and spacing of whisker fibers in composites.

Composites From Whisker Yarns

Laboratory preparation of composites from thermosetting resins, such as the lower viscosity epoxies, and vortex-spun whisker fibers is straight forward using either compression molding or simple filament winding procedures. Resin wet-out is easy, so long as yarn twist is not excessive, due to ready sorption and wicking of the uncured liquid resin by the binder fibers. Bonding between the binder material and the matrix resin is good enough under most conditions that these fibers actually behave as if they were part of the matrix itself.

The orientation distribution of reinforcing fibers and overall quality of composites prepared with vortex-spun yarns are fully equivalent to those which can be achieved by very carefully controlled flow molding. The orientation distribution of glass fibers in a typical yarn reinforced molding is shown in Table 2. Vortex yarn composites are distinguished from other systems, however, by the markedly improved fiber overlap achieved. Overlap of the fibers in these yarns is statistically uniform, while in extrusion and flow molding

processes fiber overlap is more random and depends entirely on shear forces acting on fiber bundles and matrix. The result is that the yarn reinforced composites exhibit significantly highe. tensile strengths than flow molded materials, as shown in Fig. 4. for composites of epoxy resin and 3/8 inch glass fiber (nominal length). In fact, with the exception of specially prepared model specimens, the yarn reinforced materials proved to be stronger than experimental composites of equivalent composition made by any other technique in our laboratory. Composite moduli are much less sensitive to localized discontinuities and so are roughly equivalent for both yarn reinforced and flow molded systems. The moduli of the experimental composites from Fig. 4. thus can be plotted on a common line, as shown in the comparison with "rule of mixture" values in Fig. 5.

Studies of whisker fiber composites prepared from vortex-spun yarns are still in progress and data not yet complete enough to justify publication. However, all indications to date are that improvements in composite strength are similar to those obtained in the glass systems. Reinforcement efficiencies calculated as the percentage of fiber strength utilized in the composite are much lower for the whisker reinforced systems, of course, but absolute strength markedly improved.

Acknowledgment

A number of workers in the Monsanto/Washington University Association have contributed to the work which has been described. Particular credit is due to Dr. Myrne Riley for initial development of the vortex spinning process for high modulus fiber yarns and Dr. T. B. Lewis for the data on composite properties. This work was performed by the Monsanto/ Washington University Association sponsored by the Advanced Research Projects Agency under Office of Naval Research Contract N00014-67-C-0218, formerly N00014-66-C-0045.

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TABLE 1

FIBERS USED IN YARN SPINNING

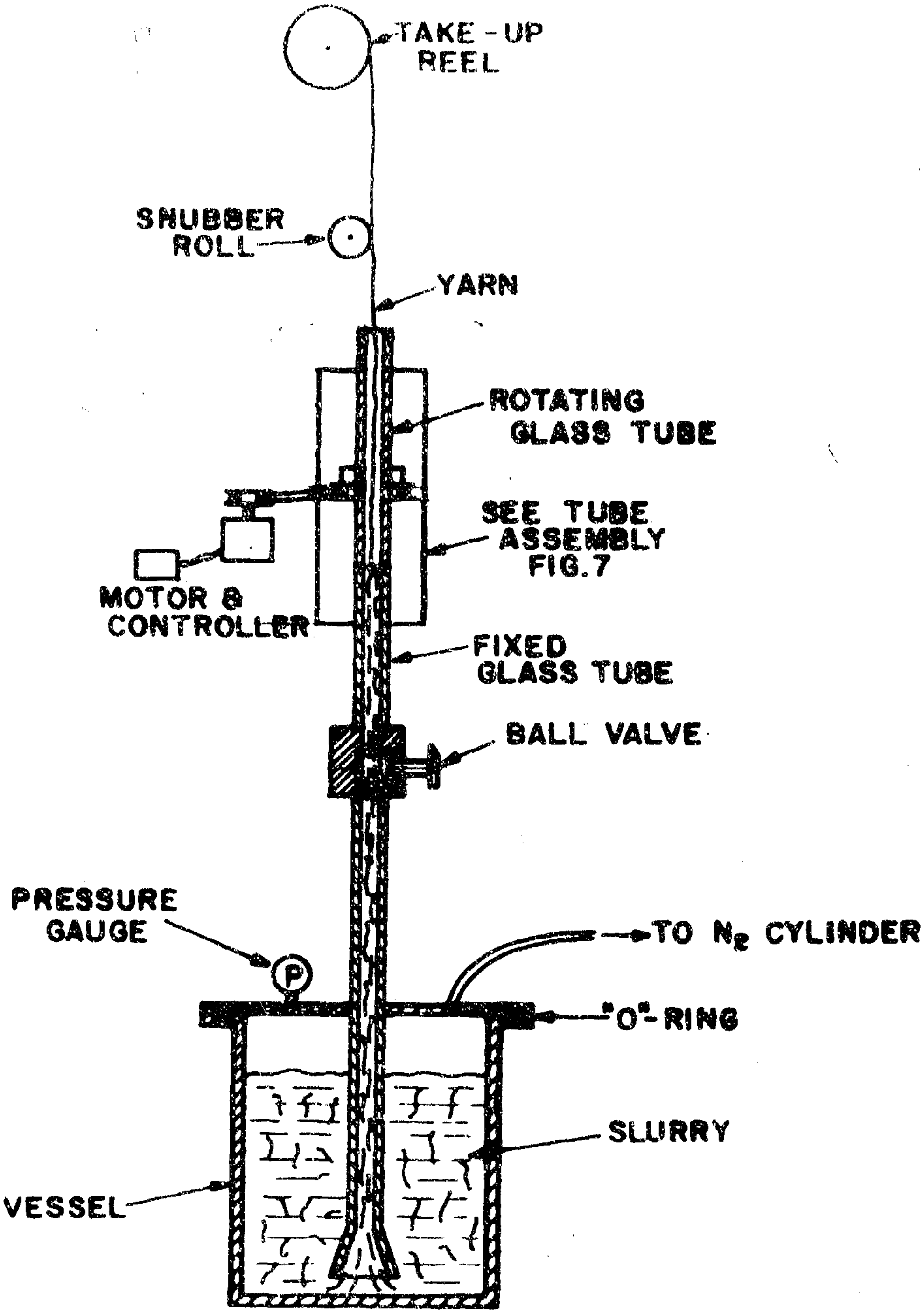
| Fiber | Average Diameter mm | Average Diameter mils |
|---|---|---|
| E-glass | 0.013 | 0.5 |
| S-glass | 0.0105 | 0.413 |
| Beta glass (Owens-Corning Fiberglas Corp.) | 0.00414 | 0.163 |
| Triacetate | 0.0239 | 0.94 |
| Acetate | 0.0211 | 0.83 |
| Acrilan 57A (Monsanto) | 0.0183 | 0.720 |
| Fortisan Rayon (Celanese) | 0.00919 | 0.36 |

TABLE 2

ORIENTATION OF GLASS FIBERS IN A TYPICAL YARN COMPOSITE

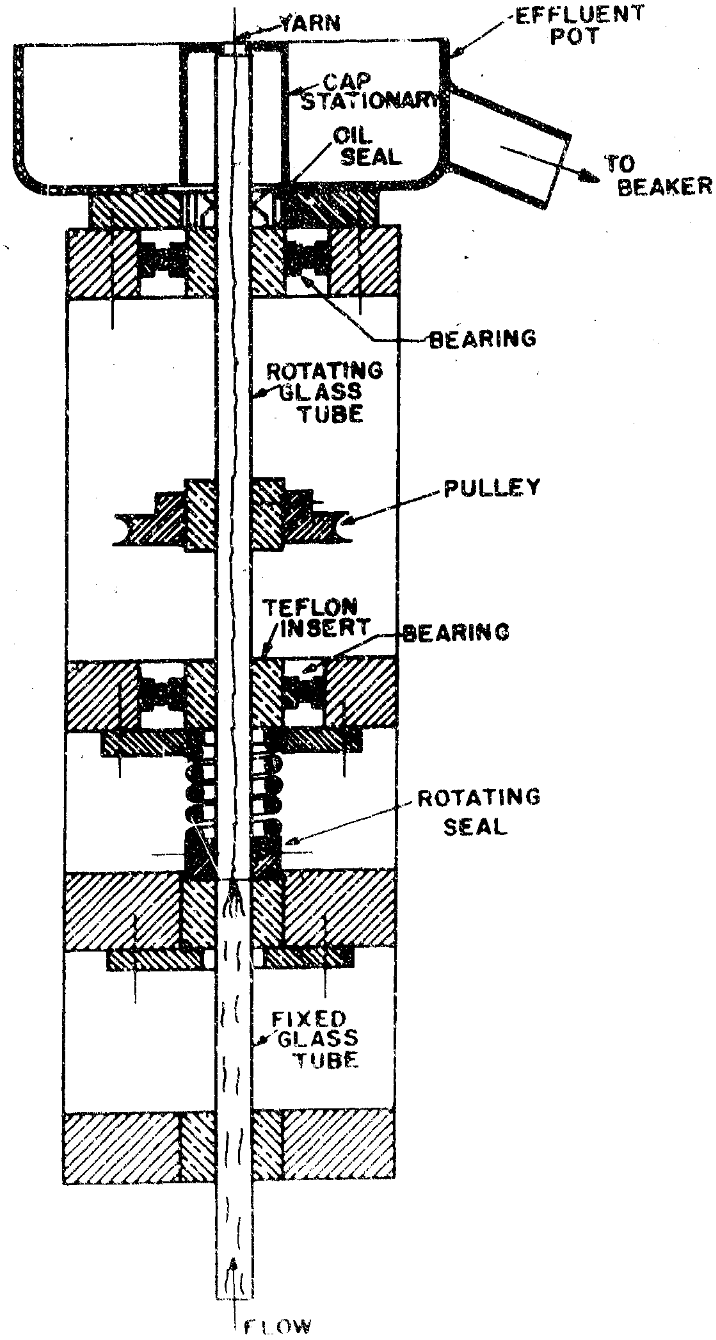
| | |
|---|---|
| Molding Technique | Hand Lay-up/Compression |
| Reinforcing Fiber | 0.163 mil E-glass |
| Matrix | Shell's Epon 828-Z |

| Angle (Degrees off Axis) | % Orientation |
|---|---|
| 0-5 | 12.5 |
| 6-10 | 10 |
| 11-15 | 12 |
| 16-20 | 11.6 |
| 21-25 | 10 |
| 26-30 | 9 |
| 31-35 | 7.7 |
| 36-40 | 3.3 |
| 41-45 | 4.2 |
| 46-50 | 2.4 |
| 51-55 | 3.9 |
| 56-60 | 2.2 |
| 61-65 | 3.4 |
| 66-70 | 1.5 |
| 71-75 | 2.9 |
| 76-80 | 1.7 |
| 81-85 | 0.7 |
| 86-90 | 1.0 |

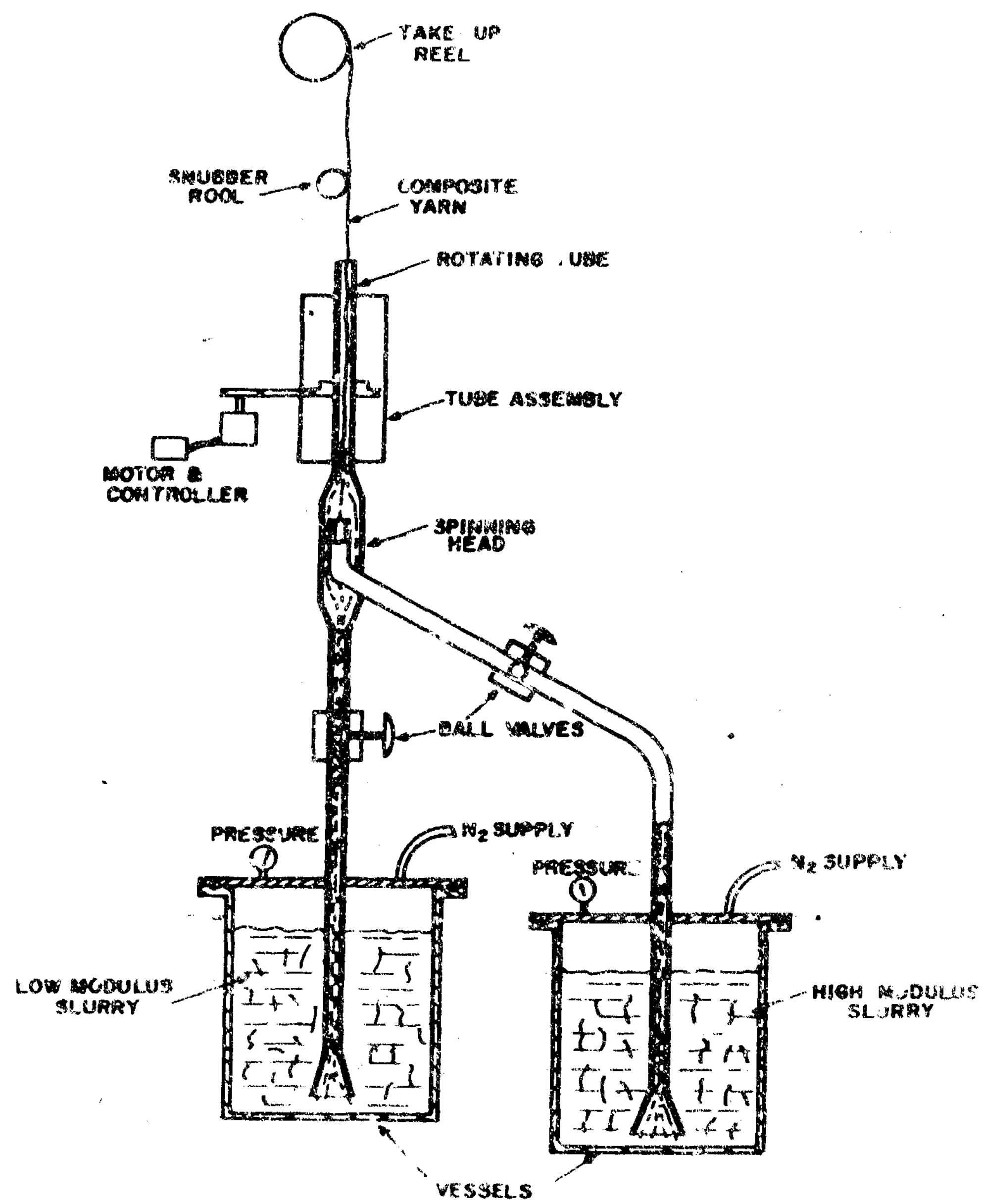



SCHEMATIC OF OPEN-END SPINNING APPARATUS

FIG. 1




ROTATING TUBE ASSEMBLY




SCHEMATIC OF OPEN-END COMPOSITE SPINNING APPARATUS

FIG. 3

FIGURE 4

VARIATION OF COMPOSITE STRENGTH WITH FIBER CONTENT

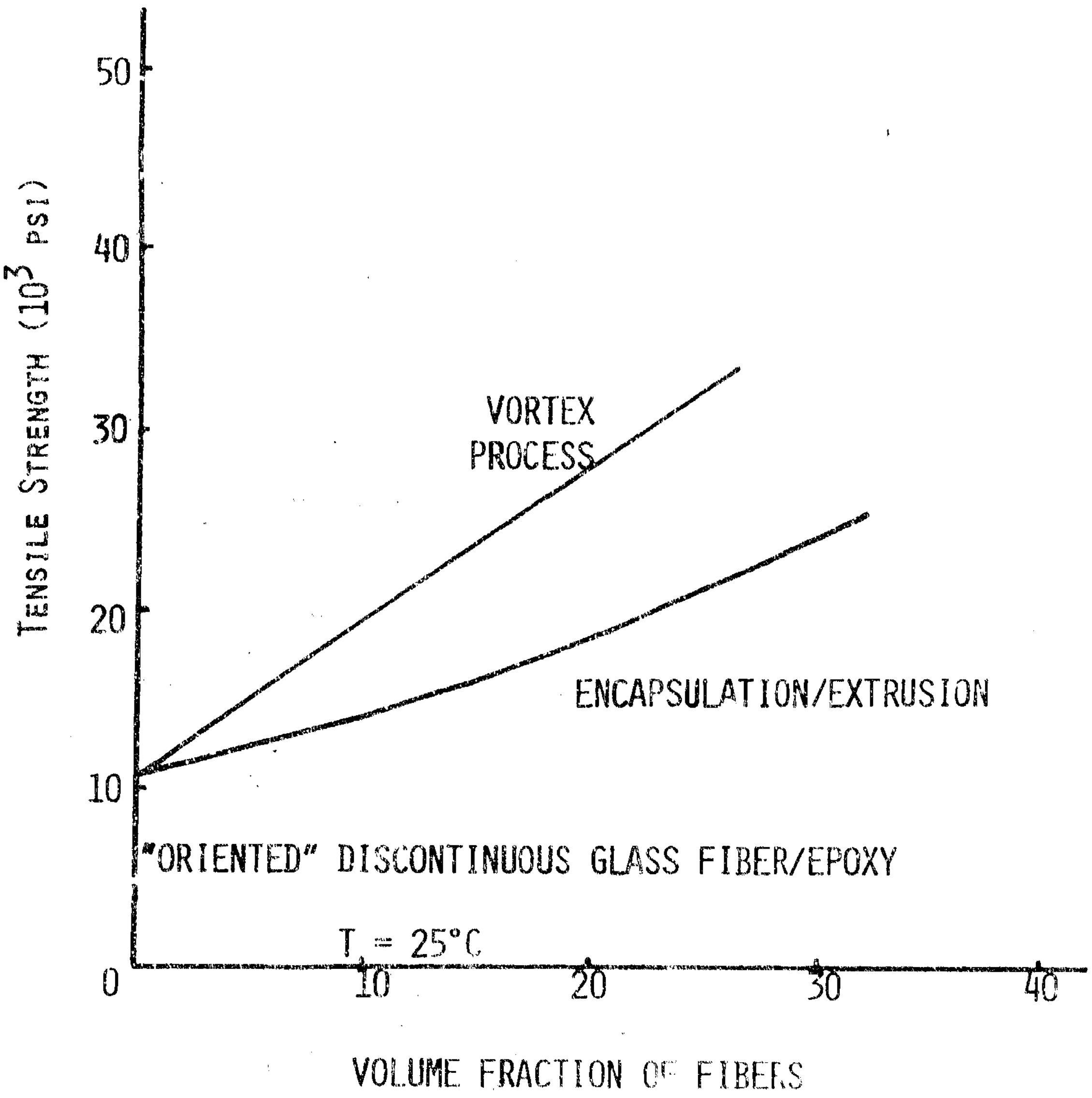
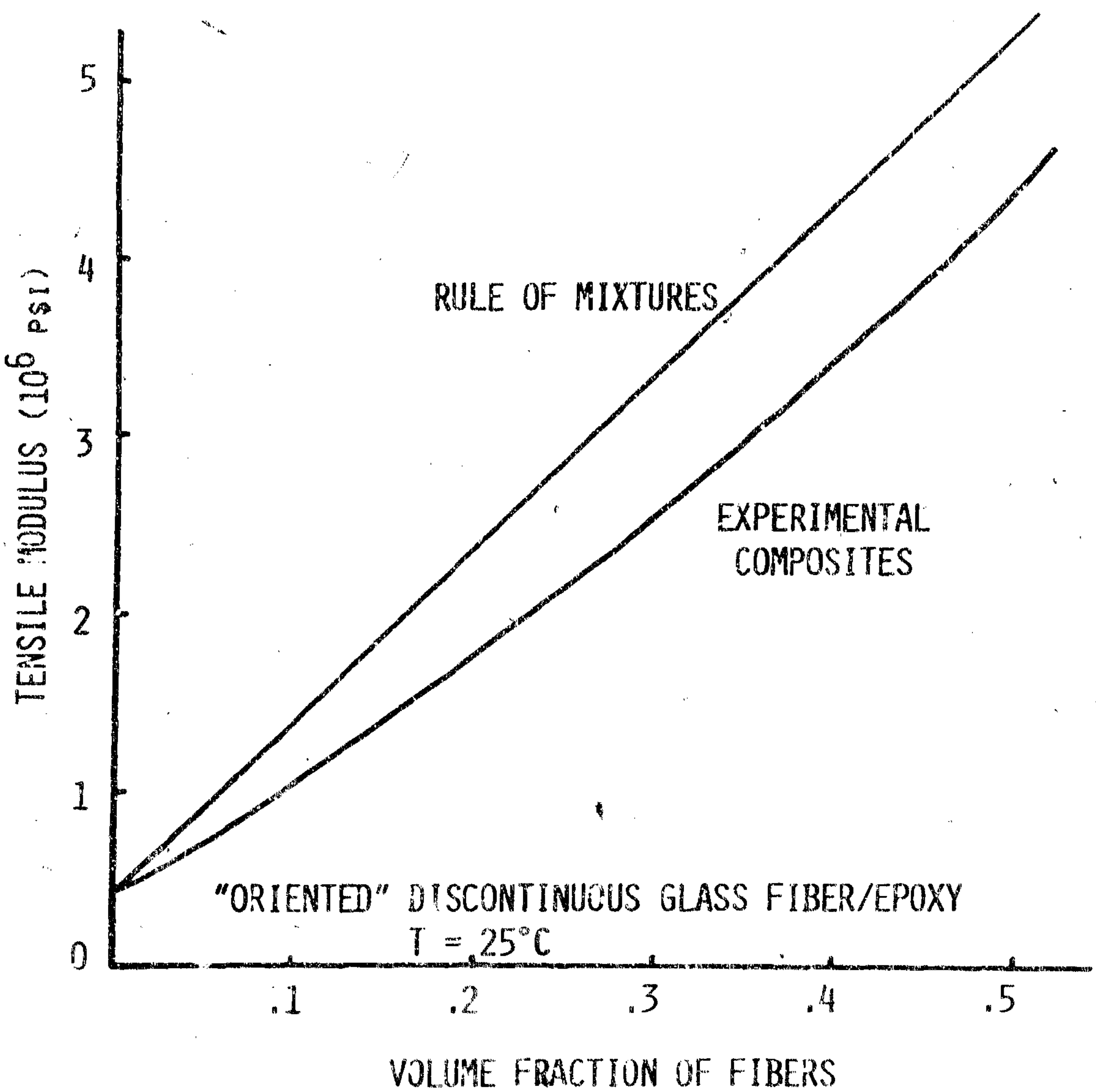


FIGURE 5

VARIATION OF COMPOSITE MODULUS WITH FIBER CONTENT



Security Classification

**DOCUMENT CONTROL DATA - R & D**

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

| | |
|---|---|
| 1. ORIGINATING ACTIVITY (Corporate author) Monsanto Research Corporation | 2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED |
| | 2b. GROUP |

3. REPORT TITLE

Controlled Orientation of Discontinuous Fibers in Composites

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (First name, middle initial, last name)

Thomas L. Tolbert, Monsanto Research Corporation

| 6. REPORT DATE | 7a. TOTAL NO. OF PAGES | 7b. NO. OF REFS |
|---|---|---|
| December 1970 | 31 | 9 |

| | |
|---|---|
| 8a. CONTRACT OR GRANT NO. N00014-67-C-0218 | 9a. ORIGINATOR'S REPORT NUMBER(S) HPC 70-121 |
| b. PROJECT NO. | |
| c. | 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) |
| d. | |

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| | |
|---|---|
| 11. SUPPLEMENTARY NOTES | 12. SPONSORING MILITARY ACTIVITY Office of Naval Research Washington, D. C. 20360 |

13. ABSTRACT

Yarns of unidirectionally oriented, discontinuous high-modulus fibers and whiskers have been successfully produced in the laboratory by a modified vortex spinning process. Both core yarns in which the higher modulus fibers are overwrapped with organic or small diameter glass fibers and all-whisker-yarns have been spun. These yarns can be readily incorporated into plastics as reinforcing agents by filament winding and related procedures. The strength of resulting composites is markedly superior to those of similar materials fabricated by other techniques due to well controlled fiber orientation and very uniform fiber overlap.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

| 14 KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| yarns | | | | | | |
| discontinuous high-modulus fibers | | | | | | |
| whiskers | | | | | | |
| vortex spinning process | | | | | | |
| glass fibers | | | | | | |
| all-whisker-yarns | | | | | | |
| plastics | | | | | | |
| reinforcing agents | | | | | | |
| filament winding | | | | | | |
| strength | | | | | | |
| fiber overlap | | | | | | |

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